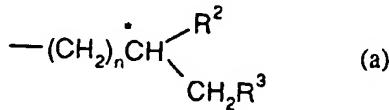
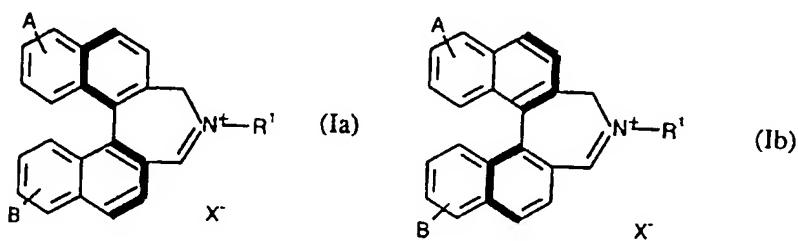




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<p>(54) Title: DINAPHTAZEPINUM SALTS USEFUL AS ENANTIOSELECTIVE FRONDS</p>		

(54) Title: DINAPHTAZEPINUM SALTS USEFUL AS ENANTIOSELECTIVE EPOXIDATION CATALYSTS



(57) Abstract

A compound of formula (Ia) or (Ib), wherein A and B each independently represents hydrogen or one, two or three naphthylidene substituents, which substituents are selected from C₁₋₆ alkyl, C₁₋₆ alkoxy, aryl, aryloxy, silyl and silyloxy; R¹ represents phenyl, C₁₋₆ alkyl, phenyl C₁₋₆ alkyl or a moiety of formula (a): wherein R² represents C₁₋₆ alkyl, phenyl or benzyl, R³ represents H or OR⁴ wherein R⁴ is C₁₋₆ alkyl or C₁₋₆ alkylsilyl and n is zero or an integer 1 or 2; and X is a counter ion; a process for the preparation of such compounds and the use of such compounds for enantioselectively epoxidising a prochiral olefin.

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DINAPHTAZEPINIUM SALTS USEFUL AS ENANTIOSELECTIVE EPOXIDATION CATALYSTS

This invention relates to novel compounds and the use of such compounds as catalysts in oxygen transfer reactions.

- 5 The catalytic asymmetric epoxidation of alkenes using chiral catalysts, in particular the salen manganese complexes of Jacobsen *et al* (International Patent Application, Publication Number WO/91/14694), is now well established methodology in asymmetric synthesis. The importance of these catalytic systems stems in the main from the versatility of application of the asymmetric
- 10 epoxidation reaction itself. This versatility is due to the many and varied nucleophiles which can be used to open the substrate epoxide providing a concomitantly varied range of enantiomerically enriched products which are increasingly required for use for the manufacture of biologically important compounds such as pesticides, herbicides and pharmaceuticals.

- 15 In addition to organo-transition metal based catalysts, such as the Jacobsen catalysts purely organic asymmetric catalysts are also known. Thus Hanquet *et al* (Tetrahedron Letters, Vol. 34, no.45, pp7271-7274) have demonstrated that the oxaziridinium salt (1S, 2R, 3R, 4S)-N-methyl-1,2-oxido-3-methyl-4-phenyl-1,2,3,4-tetrahydroisoquinolinium tetrafluoroborate catalyses the asymmetric epoxidation of *trans*-stilbene and the asymmetric oxidation of methyl p-tolyl sulphide to the corresponding sulfoxide. The oxaziridinium salts are prepared *in situ* from a catalytic amount of an iminium salt and oxone (Hanquet *et al* C.R.Acad Sci., Paris, 1991, 313,SII, pp625-628).

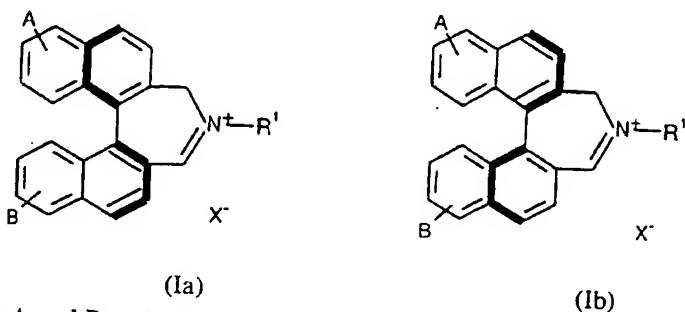
- 20 Unlike the salen manganese complexes and other organo-transition metal based catalysts, the oxaziridinium catalysts do not function by means of radical intermediates. They may therefore be used with a wider range of alkene substrates as there is no requirement for π -stabilising groups on the alkene (to stabilise incipient radicals). Also, the oxidation reactions of the oxaziridinium catalysts are stereospecific in the sense that *cis* alkenes give *cis* epoxides and *trans* alkenes give *trans* epoxides. To date however, despite these advantages, the oxaziridinium catalysts have not provided oxidation systems for use on an industrial scale.

25 It has now been discovered that a novel series of oxaziridium salts show much promise in the catalytic asymmetric epoxidation of alkenes. The catalytic

reaction employed is simple and robust enabling the use of readily available and cheap reagents as well as environmentally safe solvents.

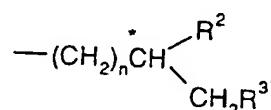
Accordingly, in a first aspect, the invention provides a compound of formula (Ia) or (Ib):

5



wherein A and B each independently represents hydrogen or one, two or three naphthylidene substituents, which substituents are selected from C₁₋₆ alkyl, C₁₋₆ alkoxy, aryl, aryloxy, silyl and silyloxy;
R¹ represents phenyl, C₁₋₆ alkyl, phenyl C₁₋₆ alkyl or a moiety of formula (a):

15



wherein R² represents C₁₋₆ alkyl, phenyl or benzyl, R³ represents H or OR⁴
wherein R⁴ is C₁₋₆ alkyl or C₁₋₆ alkylsilyl and n is zero or an integer 1 or 2;
and

X is a counter ion.

20

Suitably, A represents hydrogen.

Suitably, B represents hydrogen.

Examples of R¹ when it represents C₁₋₆ alkyl are methyl and ethyl groups.

25

An example of R₁ is benzyl.

Suitably, R² represents C₁₋₆ alkyl.

Suitably, R³ represents C₁₋₆ alkyl.

Preferably, R¹ represents C₁₋₆ alkyl,

Values for the counter ion X⁻ include BF₄⁻, Cl⁻, Br⁻, I⁻, ClO₄⁻ and PF₆⁻.

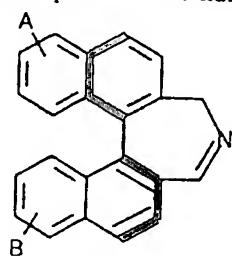
A preferred value for the counter ion X⁻ is BF₄⁻.

A suitable aryl group is a phenyl group.

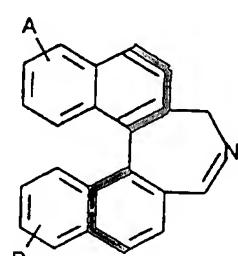
As used herein, alkyl groups, whether present alone or as part of other groups such as alkoxy or aralkyl groups, are alkyl groups having straight or branched carbon chains, containing 1 to 6 carbon atoms, e.g. methyl, ethyl,

- 5 n-propyl, iso-propyl, n-butyl, isobutyl or tert-butyl groups.

The compounds of formula (Ia) and (Ib) may be prepared by reacting, as appropriate, a compound of formula (IIa) or (IIb):



(IIa)



(IIb)

10

wherein A and B are as defined in relation to formula (I), with an alkylating agent of formula (III):



15



wherein R^1 is as defined in relation to formula (I) and L^1 is a leaving group or atom; and thereafter salting the compound produced with a source of counter ion X^- .

20

L^1 usually represents halide, such as bromide or iodide, tosyl. or mesyl.

The reaction between the compounds of formulae (II) and (III) may be carried out with or without a solvent; when using a solvent it is suitably an organic solvent, generally an inert organic solvent such as methylene dichloride, at a low to elevated temperature such as a temperature in the range of from 0 to 100°C, conveniently at ambient temperature; preferably the reaction is carried out under anhydrous conditions; preferably the reaction is carried out in an inert atmosphere, for example under nitrogen.

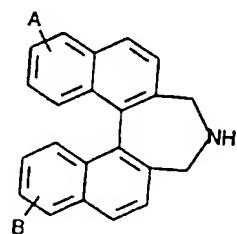
25

The salting reaction with the source of counter ion X^- may be carried out using any conventional procedure but is usually effected in the solvent used in the reaction, at ambient temperature.

The source of counter ion X^- may be any conventional source such as an appropriate metal salt and especially a silver salt, conveniently however alkylating agent (III) is also the source of counter ion X^- ; for example when preparing compounds of formula (Ia) or (Ib) wherein R¹ is C₁₋₆ alkyl and X⁻ is

- 5 BF₄⁻, the compound of formula (II) is a compound (R^{1a})₃OBF₄, wherein R^{1a} is C₁₋₆ alkyl, especially methyl.

The compounds of formula (IIa) and (IIb) may be prepared by oxidation of a chiral amine of formula (IV):



(IV)

10

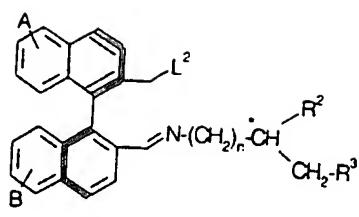
wherein A and B are as defined in relation to formula (I), suitably using potassium permanganate as oxidant in the method of Fleischhacker *et al*, monatsh chem. 1989 120 765.

- 15 The chiral compounds of formula (IV) may be prepared from the racemic compound of formula (IV) using conventional resolution methods, for example, the method disclosed by Hawkins and Fu in Journal of Organic Chemistry 1986, 51, 2820-2822.

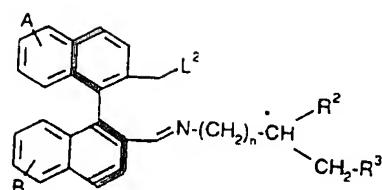
- 20 The compounds of formula (III) are known compounds or they may be prepared using methods analogous to those used to prepare known compounds, for example the methods disclosed by W. S. Johnson *et al*, Journal of American Chemical Society, 1963, 85, 1409.

- 25 The compounds of formula (IV) are known compound or they are prepared using methods analogous to those used to prepare known compounds, for example the methods disclosed by Hawkins and Fu *ibidem*.

The compounds of formula (Ia) and (Ib) wherein R¹ represents a moiety of the above defined formula (a), may be prepared, as appropriate, by cyclising a compound of formula (Va) or (Vb):



(Va)



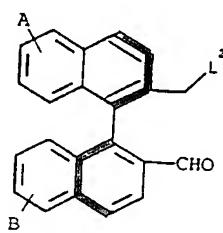
(Vb)

5 wherein A, B, R², R³ and n are as defined in relation to formula (I) and L² represents a leaving group; and thereafter salting the compound produced with a source of counter ion X⁻.

10 The cyclisation reaction of the compounds of formula (Va) and (Vb) may be carried out in an suitable organic solvent, usually an aprotic solvent such as acetone, at ambient or an elevated temperature, conveniently at the reflux temperature of the solvent.

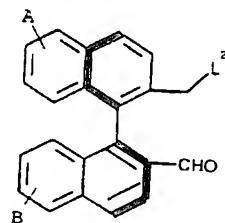
15 The salting reaction with the source of counter ion X⁻ may be carried out using any conventional procedure but is usually effected in the solvent used in the cyclisation reaction, at ambient temperature. The source of counter ion X⁻ may be any conventional source such as an appropriate metal salt, for example when X⁻ is BF₄⁻ a suitable source is an alkali metal borotetrafluoride, such as sodium tetrafluoroborate or silver tetrafluoroborate.

20 The compounds of formula (Va) and (Vb) may be prepared by reacting, as appropriate, a compound of formula (VIa) or (VIb):



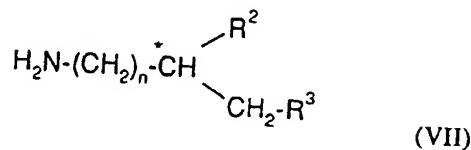
25

(VIa)



(VIb)

wherein A, B and L² are as defined in relation to formula (V_a), with a compound of formula (VII):

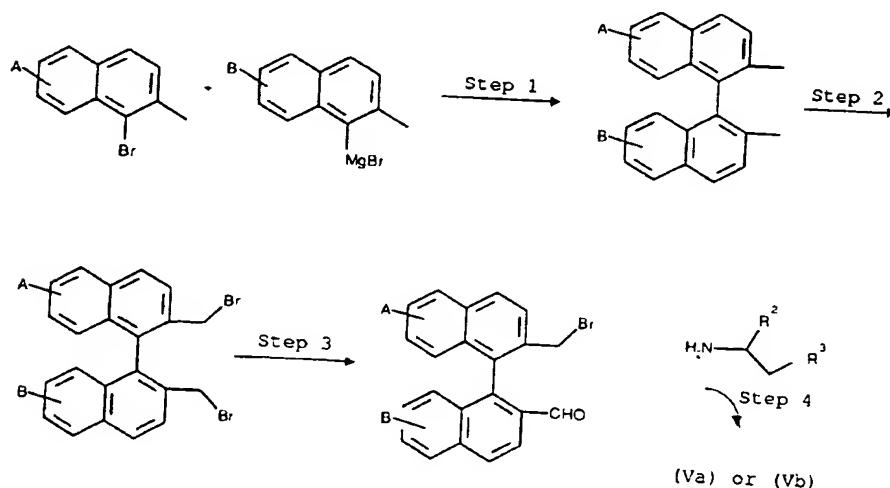


wherein R², R³ and n are as defined in relation to formula (I).

The reaction between the compound of formula (VIa) or (VIb) and the compound of formula (VII) may be carried out using any suitable organic solvent, generally an aprotic solvent such as tetrahydrofuran, usually at a low or medium 10 elevated temperature such as a temperature in the range of from -78 to 50°C.

The compounds of formula (VII) are known compound or they may be prepared using methods analogous to those used to prepare known compounds, for example the methods disclosed by Evans *et al*, Organic Synthesis, Vol. 68, 1989, 77

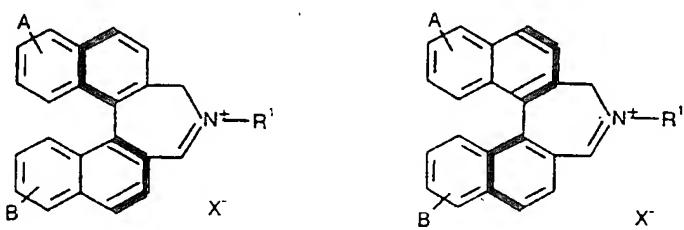
15 The compounds of formula (VIa) and (VIb) may be prepared in accordance with methods illustrated below:



wherein A and B are as defined in relation to formula (I), the conditions of reaction and reagents used in for Steps 1 to 4 being those found in the following references:

- 5 Steps 1 and 2: N. Naigrot, J.P. Mazaleyrat, Synthesis, 1985, p 317.
Step 3: H. B. Hass, M.L.Bender, Org. Syn., Coll. Vol. 4, 1963, 932.
Step 4: B. Bezas, L. Zervas, JACS, 1961, 83, 719

As stated above the compounds of formula (I) are useful catalysts in the asymmetric epoxidation of alkenes. Accordingly, in a further aspect the invention provides a process for enantioselectively epoxidising a prochiral olefin such as 1-phenylcyclohexene, 1-methylcyclohexene, trans-stilbene and methylstilbene, which process comprises reacting the prochiral olefin with a nucleophilic oxidising agent in the presence of a catalyst, characterised in that the catalyst is a compound of formula (Ia) or (Ib);

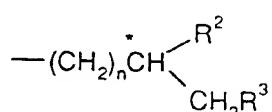


(Ia)

(Ib)

wherein A and B each independently represents hydrogen or one, two or three naphthylidene substituents, which substituents are selected from C₁₋₆ alkyl, C₁₋₆ alkoxy, aryl, aryloxy, silyl and silyloxy;

R^1 represents phenyl, C_{1-6} alkyl, phenyl C_{1-6} alkyl or a moiety of formula (a):



- 25 wherein R² represents C₁₋₆ alkyl, phenyl or benzyl;
R³ represents H or OR⁴ wherein R⁴ is C₁₋₆ alkyl or C₁₋₆ alkylsilyl and n is zero or an integer 1 or 2; and
X is a counter ion.

One suitable nucleophilic oxidising agent is provided by a mixture of oxone (KHSO_5) and NaHCO_3 .

- 5 The epoxidation reaction may be carried out using any suitable procedure wherein the prochiral olefin, the nucleophilic oxidising agent and the compound of formula (Ia) or (Ib) are allowed to react thereby providing the required epoxide.

The reaction is carried out in an organic solvent such as acetonitrile, dimethylsulphoxide, dimethylformamide or pyridine or in an organic solvent/water mixture such as aqueous acetonitrile.

- 10 Aqueous acetonitrile is a particularly apt reaction solvent when oxone/ NaHCO_3 is the nucleophilic oxidising agent.

The reaction is carried out at a low to medium-elevated temperature such as a temperature in the range of from -20 to 50°C, preferably at ambient temperature.

- 15 Suitably, the reaction is carried out at a neutral or alkaline pH such as in the range of from pH 7 to 14, preferably it is carried out in the range of from pH 8 to 10.

- 20 Suitably the molar ratio of the compound of formula (Ia) or (Ib) to the prochiral olefin is in the range of from 1 to 20 mol %, preferably in the range of from 5 to 10 mol %.

The following preparation and examples illustrate the present invention.

Iminium Salt Catalysts

General Preparation Procedure:

To a solution of the required imine in CH_2Cl_2 was added the corresponding alkylating agent. The reaction was left to react at room temperature until completion. The solvent was then removed and the residue was precipitated out in ether to give the desired salt.

Example 1: (*S*-(+)-5,5-Dihydro-2*H*-dinaphth[2,1-*c*:1',2'-*e*]-N-methyl azepine Tetrafluoroborate

To a solution of (*S*)-imine from Preparation 1 (400mg, 1.36 mmol) in dry CH_2Cl_2 (10 ml) was added under N_2 , Me_3OBF_4 (222mg, 1.5 mmol) in one portion. The reaction was left to react at room temperature under N_2 for 24h. The solvent was removed and the residue was precipitated out in ether to give the desired salt (518 mg, 96%), $[\alpha]_D^{20+} 1070$ (c 1.1 in CH_2Cl_2); δ_{H} (250 MHz; CDCl_3) 4.05 (3H, s, CH_3), 4.6 (1 H, d, J 12.5 Hz, $\text{ArCH}'\text{H}$), 4.95 (1 H, d, J 12.5Hz, $\text{ArCH}'\text{H}$), 7.0-8.25 (12 H, m, Ar-H), and 9.2 (1 H, s, $\text{CH}=\text{N}$); δ_{C} (62 MHz; CDCl_3) 48.76, 58.8, 125.29, 126.14, 126.78, 126.9, 127.12, 127.21, 127.5, 128.68, 129.54, 129.67, 130.12, 130.89, 131.41, 131.78, 131.93, 133.87, 135.29, 141.12, and 168.36; m/z (FAB) 308 (M^+-87 , 100%) (Found 308.1448. $\text{C}_{23}\text{H}_{18}\text{N}$ requires 308.1439).

Example 2: (*S*)-(+)5,5-Dihydro-2*H*-dinaphth[2,1-*c*:1',2'-*e*]-N-methyl azepine iodide

A solution of (*S*)-imine from Preparation 1 (50 mg, 0.17 mmol) in iodomethane (2 ml) was stirred at room temperature, and very soon a yellow solid was formed in the reaction mixture. TLC of the reaction after 24 h showed only a small amount of starting material left. The remaining imine and excess of iodomethane were removed by trituration with ether. After drying under high vacuum the desired compound was obtained as a yellow solid (72 mg, 97%); δ_{H} (250 MHz; CDCl_3) 4.25 (3 H, s, CH_3), 4.70 (1 H, d, J 13.1 Hz, $\text{ArCH}'\text{H}$), 4.85 (1 H, d, J 13.1 Hz, $\text{ArCH}'\text{H}$), 7.00-8.50 (12 H, m, Ar-H), and 10.50 (1 H, s, $\text{N}=\text{CH}$).

Example 3: (*S*)-(+)5,5-Dihydro-2*H*-dinaphth[2,1-*c*:1',2'-*e*]-N-methyl azepine perchlorate

A solution of AgClO_4 (34.3 mg, 0.17 mmol) in acetone (1 ml) was added to a solution of (*S*)-iminium salt from Example 2 (72 mg, 0.16 mmol) in CH_2Cl_2 (1 ml). The solid formed was filtered off and the filtrate was concentrated to give

the desired iminium salt which was precipitated from ether. After drying under high vacuum the desired compound was obtained as a yellow solid (60 mg, 90%), [α]D²⁰ + 769 (c 1.09 in acetone); δ _H (250 MHz; CDCl₃) 4.15 (3 H, s, CH₃), 4.70 (1 H, d, J 13 Hz, ArCH'H), 4.80 (1 H, d, J 13 Hz, ArCH'H'), 7.0-8.2 (12 H, m, Ar-H), and 9.35 (1 H, s, N=CH); δ _C (100 MHz; d₆-acetone) 49.44, 59.19, 126.59, 126.64, 127.62, 127.85, 127.93, 128.03, 128.46, 129.58, 129.60, 130.01, 130.24, 130.26, 130.91, 131.76, 132.18, 132.40, 132.82, 134.83, 136.92, 141.86, and 169.98.

10 **Example 4: (R)-(-)-5,5-Dihydro-2H-dinaphth[2,1-c:1',2'-e]-N-methyl azepine hexfluorophosphate**

A solution of AgPF₆ (40.7 mg, 0.16 mmol) in acetone (1 ml) was added to a solution of (R)-iminium salt from Example 2 (70 mg, 0.16 mmol) in CH₂Cl₂ (2 ml). The solid formed was filtered off and the filtrate was concentrated to give the desired iminium salt which was precipitated from ether. After drying under high vacuum the desired compound was obtained as a yellow solid (65 mg, 92%), [α]D²⁰-778 (c 1.25 in acetone); δ _H (250 MHz; CDCl₃) 4.09 (3 H, s, CH₃), 4.64 (1 H, d, J 13 Hz, ArCH'H), 4.89 (1 H, d, J 13 Hz, ArCH'H'), 7.00-8.25 (12 H, m, Ar-H), and 9.12 (1 H, s, N=CH); δ _C (100 MHz; CD₂Cl₂) 49.22, 59.60, 125.17, 125.95, 126.67, 127.42, 127.52, 127.82, 128.18, 129.02, 129.07, 129.96, 130.24, 130.97, 131.42, 131.94, 32.37, 132.44, 134.37, 135.02, 135.92, 142.19, and 168.56.

25 **Example 5: (S)-(+)-5,5-Dihydro-2H-dinaphth[2,1-c:1',2'-e]-N-ethyl azepine Iodide**

A solution of (S)-imine from Preparation 1 (50 mg, 0.17 mmol) in iodoethane (2 ml) was stirred at room temperature, a yellow solid was soon formed in the reaction mixture. TLC of the reaction after 24 h showed that only a small amount of starting material was left. The remaining imine and excess iodoethane were removed by trituration with ether. After drying under high vacuum the desired product was obtained as a yellow solid (60 mg, 98%), m.p. >200 °C (dec.), [α]D²⁰ + 878 (c 0.41 in CH₂Cl₂); δ _H (250 MHz; CDCl₃) 1.51 (3 H, t, J 7 Hz, CH₃), 4.45-4.75 (2 H, m, CH₂CH₃), 4.6 (1 H, d, J, 12.5 Hz, ArCH'H), 4.95 (1 H, d, J 12.5 Hz, ArCH'H'), 7.00-8.60 (12 H, m, Ar-H), and 10.60 (1 H, s, N=CH); δ _C (100 MHz; CD₂Cl₂) 14.30, 57.75, 57.86, 125.21, 127.09, 127.42, 127.62, 127.68, 127.89, 128.93, 129.04, 129.75, 129.84, 130.62, 131.72, 131.93, 132.04, 132.45, 134.23, 135.41, 135.80, 141.95, and 168.23; m/z (FAB) 323 (M⁺-128), 322 (M⁺-129, 100%), and 308 (M⁺-141); HRMS: m/z calc. 322.1604. C₂₄H₂₀N (M⁺-127) found 322.1596.

5 **Example 6: (*R*)-(-)-5,5-Dihydro-2*H*-dinaphth[2,1-*c*:1',2'-*e*]-N-ethyl azepine Tetrafluoroborate**

A solution of AgBF₄ (40 mg, 0.2 mmol) in acetone (1 ml) was added to a solution of the (*R*)-iminium salt from Example 5 (76 mg, 0.17 mmol) in CH₂Cl₂ (2 ml). The solid (AgI) formed was removed by filtration. The resulting foam, obtained by concentration of the filtrate, was triturated with ether to give the desired product as a yellow gum (59 mg, 84%); [α]_D²⁰ - 832 (c 0.87 in acetone); δ_H (250 MHz; CD₂Cl₂) 1.50 (3 H, t, *J* 6.5 Hz, CH₃), 4.25 (2 H, q, *J* 6.5 Hz, CH₂CH₃), 4.53 (1 H, d, *J* 13 Hz, ArCH'H), 4.94 (1 H, d, *J* 13 Hz, ArCHH'), 6.9-8.15 (12 H, m, Ar-H), and 9.13 (1 H, s, N=CH); δ_C (100 MHz; CD₂Cl₂) 13.87, 57.49, 58.38, 125.46, 126.33, 126.88, 127.02, 127.10, 127.15, 127.86, 128.86, 128.97, 129.67, 129.97, 130.64, 131.60, 131.87, 132.01, 132.40, 134.25, 135.82, 141.86, and 167.90

10 **Example 7: (*S*)-(+)-5,5-Dihydro-2*H*-dinaphth[2,1-*c*:1',2'-*e*]-N-benzyl azepine Bromide**

15 A solution of (*S*)-imine from Preparation 1 (50 mg, 0.17 mmol) in benzyl bromide (2 ml) was left to stir at room temperature for 2 days. TLC of the reaction showed a small amount of starting material left. Excess benzyl bromide was removed under vacuum and the residue was triturated with ether to remove the unreacted starting material and trace amounts of benzyl bromide. After 20 drying under high vacuum the desired compound was obtained as a yellow solid (75 mg, 95%), m.p. 150-152 °C (dec.), [α]_D²⁰ + 450 (c 1.48 in CH₂Cl₂); δ_H (250 MHz; CDCl₃) 4.45 (1 H, d, *J* 13.4 Hz, ArCH'H), 4.90 (1 H, d, *J* 13.4 Hz, ArCHH'), 5.80 (1 H, d, *J*, 13.0 Hz, PhCH'H), 5.94 (1 H, d, *J* 13.0 Hz, PhCHH'), 6.75-8.6 (17 H, m, Ar-H), and 11.22 (1 H, s, N=CH); δ_C (100 MHz; CDCl₃) 25 56.55, 65.28, 124.68, 126.86, 126.94, 127.19, 127.44, 128.47, 128.65, 128.74, 30 128.97, 129.35, 129.49, 129.87, 130.19, 130.90, 131.03, 131.45, 131.60, 133.44, 135.34, 141.42, and 169.45; m/z (FAB) 385 (M⁺-79), 384 (M⁺-80, 100%); HRMS: m/z calc. 384.1745 C₂₉H₂₂N (M⁺-80) requires 384.1752.

35 **Example 8: (*R*)-(-)-5,5-Dihydro-2*H*-dinaphth[2,1-*c*:1',2'-*e*]-N-benzyl azepine Tetrafluoroborate**

To a solution of (*R*)-bromide salt from Example 7 (prepared from 50 mg, 0.17 mmol of (*R*)-imine from Preparation 1) in CH₂Cl₂ (2 ml) was added AgBF₄ (40 mg, 0.2 mmol). The solid (AgBr) formed was separated and the filtrate

concentrated. The resulting foam was triturated with ether to give the desired product as a yellow gum (48 mg, 60%); $[\alpha]_D^{20} - 637$ (c 0.6 in acetone); δ_H (250 MHz; CDCl₃) 4.55 (1 H, d, J 12.5 Hz, ArCH'H), 4.95 (1 H, d, J 12.5 Hz, ArCH'H), 5.48 (1 H, d, J 14 Hz, PhCH'H), 5.58 (1 H, d, J 13 Hz, PhCH'H), 6.65-8.16 (17 H, m, Ar-H), and 9.55 (1 H, s, N=CH); δ_C (100 MHz; CDCl₃) 56.54, 66.12, 124.71, 126.60, 126.63, 126.92, 127.14, 127.51, 128.50, 128.66, 129.43, 129.47, 129.70, 130.01, 130.18, 130.29, 130.64, 130.95, 131.05, 131.45, 131.60, 133.46, 135.41, 135.44, 141.56, and 168.17.

10

Catalytic Epoxidation using Iminium Salt Catalysts

General Procedure

To a solution of alkene (0.5 mmol) in a mixture of acetonitrile (4.5 ml) and water (1-2 drops) were added first finely crushed NaHCO₃ (2 mmol) and oxone (0.5 mmol) then the catalyst (0.05 mmol or 0.025 mmol). The resulting yellow suspension was allowed to react at room temperature, under good stirring. The reaction was monitored using thin layer chromatography (TLC). Usually towards the end of the reaction the colour of the mixture changed from bright yellow to nearly colourless. Water was added to the reaction mixture followed by extraction into methylene dichloride. The organic extracts were combined and dried over anhydrous sodium sulphate. Concentration on a rotary evaporator gave a material which was purified (column chromatography) to give the desired epoxide.

25

Example 1: Preparation of Phenyl cyclohexene oxide

To a solution of phenyl cyclohexene (79mg, 0.5 mmol) in a mixture of acetonitrile (4.5 ml) and water (2 drops) were added first finely crushed NaHCO₃ (168 mg, 2mmol) and oxone (307 mg, 0.5 mmol) then the catalyst (0.05 mmol). The resulting yellow suspension was allowed to react at RT, under good stirring. TLC was used to follow the reaction which indicated that the reaction was finished in 2 h . Water (3 ml) was added to the reaction mixture followed by extraction into methylene dichloride. The organic extracts were combined and dried over anhydrous sodium sulphate. Concentration on a rotary evaporator gave a material which was purified on a column using 2% ethyl acetate : petrol

mixture as eluent to give the desired compound as a colourless oil. (72mg, 83% yield, 70% e.e.).

The epoxidation of phenyl cyclohexene to phenyl cyclohexene oxide was then carried out using other catalysts of the invention. The results obtained are shown
5 in Table 1

Table 1

Example No.	R ¹	X	Yield %	ee %
1	Me	BF ₄	83	70
3	Me	ClO ₄	54	74
4	Me	PF ₆	48	61
5	Et	I	55	78
6	Et	BF ₄	78	76
7	Bn	Br	71	74
8	Bn	BF ₄	78	73

Preparation 1: (R(-) and S(+) 5,5-Dihydro-2H-dinaphth[2,1-c:1',2'-e]azepine

To a solution of (R)- or (S)-amine (295 mg, 1 mmol) (Journal of Organic Chemistry, 1986, 51, 2820-2822) in THF (5ml) was added KMnO₄ (648 mg, 4 mmol). The reaction was allowed to react at room temperature for 5 h before the solid was removed by filtration. Concentration of the filtrate followed by purification on column using ethyl acetate : petrol (1:1) as eluant gave the desired compound as a syrup (234 mg, 80%).

(S)- isomer, $[\alpha]_D^{20} +1363.7$, (c 1.19 in CH₂Cl₂);

(R)- isomer, $[\alpha]_D^{20} -1363.7$, (c 1.19 in CH₂Cl₂);

Both isomers: δ_H (250 MHz; CDCl₃) 3.95 (1 H, dd, J 2.2 Hz and 11 Hz,

ArCH'H), 4.96 (1 H, d, J 11 Hz, ArCH'H'), 7.0-8.1 (12 H, m, Ar-H), and 8.6 (1 H, d, J 2.2 Hz, CH=N); δ_C (62 MHz; CDCl₃) 55.90, 124.36, 125.27, 125.87, 126.05, 126.42, 126.69, 127.16, 127.49, 128.07, 128.25, 128.44, 129.18, 130.49,

131.70, 132.08, 132.34, 132.99, 135.04, 136.99, 140.96, and 162.47; m/z (FAB)
294 ($M^{+}+1$, 100%), 154 ($M^{+}-139$), and 136 ($M^{+}-157$) (Found
294.1275. $C_{22}H_{16}N$ requires 294.1283).

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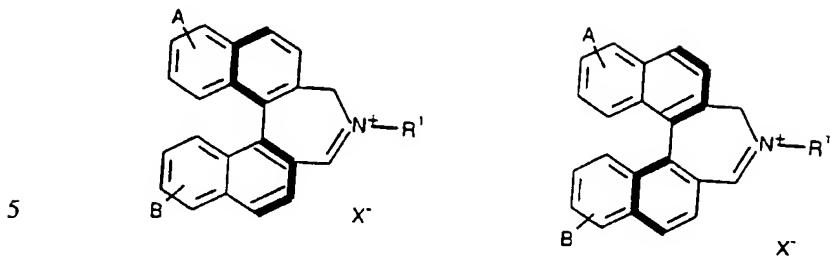
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Claims:

1. A compound of formula (Ia) or (Ib):

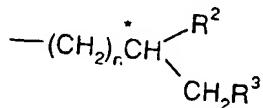


(Ia)

(Ib)

wherein A and B each independently represents hydrogen or one, two or three naphthylidene substituents, which substituents are selected from C₁₋₆ alkyl, C₁₋₆

- 10 alkoxy, aryl, aryloxy, silyl and silyloxy;
R¹ represents phenyl, C₁₋₆ alkyl, phenyl C₁₋₆ alkyl or a moiety of formula (a):



- 15 wherein R² represents C₁₋₆ alkyl, phenyl or benzyl, R³ represents H or OR⁴
wherein R⁴ is C₁₋₆ alkyl or C₁₋₆ alkylsilyl and n is zero or an integer 1 or 2;
and

X is a counter ion.

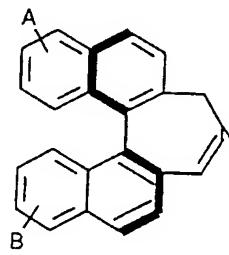
- 20 2. A compound according to claim 1, wherein A represents hydrogen and B
represents hydrogen.

3. A compound according to claim 1 or claim 2, wherein R¹ represents C₁₋₆
alkyl

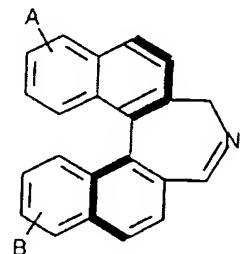
- 25 4. A compound according to any one of claims 1 to 3, wherein R¹ represents
C₁₋₆ alkyl.

5. A compound according to any one of claims 1 to 4, wherein R¹ represents
methyl or ethyl.

6. A compound according to any one of claims 1 to 5, wherein counter ion X^- is selected from the list consisting of: BF_4^- , Cl^- , Br^- , I^- , ClO_4^- and PF_6^- .
7. A compound according to any one of claims 1 to 6, wherein counter ion X^- is BF_4^- .
8. A compound according to claim 1, selected from the list consisting of: (S)-(+)-5,5-dihydro-2H-dinaphth[2,1-c:1',2'-e]-N-methyl azepine tetrafluoroborate;
- 10 (S)-(+)-5,5-dihydro-2H-dinaphth[2,1-c:1',2'-e]-N-methyl azepine iodide; (S)-(+)-5,5-dihydro-2H-dinaphth[2,1-c:1',2'-e]-N-methyl azepine perchlorate; (R)-(-)-5,5-dihydro-2H-dinaphth[2,1-c:1',2'-e]-N-methyl azepine hexfluorophosphate;
- (S)-(+)-5,5-dihydro-2H-dinaphth[2,1-c:1',2'-e]-N-ethyl azepine iodide;
- 15 (R)-(-)-5,5-dihydro-2H-dinaphth[2,1-c:1',2'-e]-N-ethyl azepine tetrafluoroborate; (S)-(+)-5,5-dihydro-2H-dinaphth[2,1-c:1',2'-e]-N-benzyl azepine bromide; and (R)-(-)-5,5-dihydro-2H-dinaphth[2,1-c:1',2'-e]-N-benzyl azepine tetrafluoroborate.
9. A process for the preparation of the compounds of formula (Ia) and (Ib)
- 20 which process comprises reacting, as appropriate, a compound of formula (IIa) or (IIb):



(IIa)



(IIb)

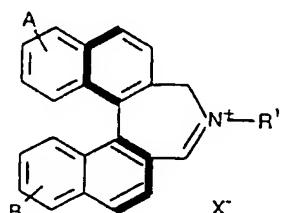
25 wherein A and B are as defined in relation to formula (I), with an alkylating agent of formula (III):



(III)

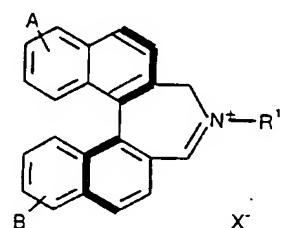
wherein R¹ is as defined in relation to formula (I) and L¹ is a leaving group or atom; and thereafter salting the compound produced with a source of counter ion X⁻.

10. A process for enantioselectively epoxidising a prochiral olefin which
 5 process comprises reacting the prochiral olefin with a nucleophilic oxidising agent in the presence of a catalyst, characterised in that the catalyst is a compound of formula (Ia) or (Ib):



10

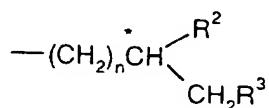
(Ia)



(Ib)

wherein A and B each independently represents hydrogen or one, two or three naphthylidene substituents, which substituents are selected from C₁₋₆ alkyl, C₁₋₆ alkoxy, aryl, aryloxy, silyl and silyloxy;

- 15 R¹ represents phenyl, C₁₋₆ alkyl, phenyl C₁₋₆ alkyl or a moiety of formula (a):



- 20 wherein R² represents C₁₋₆ alkyl, phenyl or benzyl;
 R³ represents H or OR⁴ wherein R⁴ is C₁₋₆ alkyl or C₁₋₆ alkylsilyl and n is zero or an integer 1 or 2; and
 X is a counter ion.

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INTERNATIONAL SEARCH REPORT

Inte	rnal Ap	No
PCT/EP 96/03551		

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07D223/14 C07F7/08 C07D301/03 C07B53/00

According to International Patent Classification (IPC) or to both national classification and IPC

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	TETRAHEDRON LETTERS, vol. 34, no. 45, 1993, OXFORD GB, pages 7271-4, XP002020018 L. BOHÉ ET AL.: "The stereospecific synthesis of a new chiral oxaziridinium salt" cited in the application see the whole document ---	1-10
Y	TETRAHEDRON LETTERS, vol. 24, no. 12, 1983, OXFORD GB, pages 1243-6, XP002020019 J.P. MAZALEYRAT: "Méthode simple de synthèse d'agents de transfert chiraux par action d'un agent alkylant à squelette binaphytyle-1,1'" see the whole document ---	1-10 -/-

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2 December 1996

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INTERNATIONAL SEARCH REPORT

International Application
PCT/EP 96/03551

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim No.
Category	Citation of document, with indication, where appropriate, of the relevant passages	
Y	US 5 360 568 A (S.A. MADISON ET AL.) 1 November 1994 see the whole document	1-10
P,X	--- CHEMICAL COMMUNICATIONS, no. 2, January 1996, CAMBRIDGE GB, pages 191-2, XP002020020 V. K. AGGARWAL ET AL.: "Catalytic asymmetric synthesis of epoxides mediated by chiral iminium salts" see the whole document -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members			International Application No. PCT/EP 96/03551	
Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
US-A-5360568	01-11-94	AU-A- 8060994 WO-A- 9513352 EP-A- 0728182 US-A- 5482515 US-A- 5550256 ZA-A- 9408978	29-05-95 18-05-95 28-08-96 09-01-96 27-08-96 13-05-96	

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(54) Title: IMPROVEMENTS RELATING TO BLEACHING COMPOSITIONS COMPRISING HYDROGEN PEROXIDE

(57) Abstract

The invention provides a bleaching composition of pH 10-14 which comprises an oxygen transfer agent and hydrogen peroxide. It is believed that the reaction of hydrogen peroxide with the imine quat oxygen transfer agents proceeds through a different route than that of the organic and inorganic peroxides. As a consequence, the formation of acyl hydroxamate is significantly reduced. Furthermore it is believed that when hydrogen peroxide is used as the bleaching agent in the pH range indicated, a surprising improvement in the efficacy of the bleaching system occurs and it is possible to formulate peroxide based systems which have efficacy approaching or exceeding that of hypochlorite without the disadvantages associated with hypochlorite. A further aspect of the present invention provides a method for bleaching a stained substrate which comprises the step of treating the substrate with a bleaching composition of pH 10-14, which bleaching composition comprises an oxygen transfer agent and hydrogen peroxide.

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- 1 -

IMPROVEMENTS RELATING TO BLEACHING COMPOSITIONS
COMPRISING HYDROGEN PEROXIDE

5

Field of the Invention

The present invention relates to bleaching compositions comprising hydrogen peroxide.

10

Background to the Invention

In household cleaning, fabric washing and in many other areas there is a general need for agents which can 'bleach' unsightly materials, i.e. which can react with these materials to decolourise them. One of the commonest of such bleaching agents is sodium hypochlorite, which is widely used in cleaning compositions to decolourise soils, to assist in cleaning through its reaction with soils and to kill micro-organisms.

Sodium hypochlorite is a powerful oxidising agent, which can decolourise a very large number of coloured compounds found in soils but which has significant limitations when used to bleach certain fatty and pyrolysed soils. Many consumers prefer not to use chlorine-based bleach compounds due to the characteristic and pungent smell of chlorine. In some circumstances the use of a chlorine containing bleaching composition must be avoided due to the possibly adverse effects of mixing such compositions with acidic bathroom cleaners and the resulting release of chlorine gas.

35

- 2 -

There is a need for an alternative to chlorine-based bleaching and bleaching/cleaning agents. One well known class of alternatives are the peroxygen compounds. While these have been used extensively as
5 bleaching and cleaning agents, the efficacy of peroxygen compounds as bleaching agents falls short of that of hypochlorite. There is therefore a general need to find new alternatives to chlorine based bleaching agents and to improve the properties of
10 these towards that of hypochlorite.

It is known to use oxygen transfer agents such as 'imine quat' compounds to promote the bleaching activity of peroxygen compounds. In the context of
15 the present invention, an oxygen transfer agent is a species which reacts with a peroxygen compound such as hydrogen peroxide to form an oxidative bleaching species which oxidative bleaching species, subsequently reacts with a substrate to regenerate the
20 oxygen transfer agent.

Such oxygen transfer agents include N-methyl-3,4-dihydroisoquinolinium salts. US 5360569 discloses that imine quat molecules can be used to promote the
25 activity of TAED/perborate bleaching compositions. These systems are believed to work by generating peracetic acid in situ. This organic peroxide is believed to interact with the imine quat. to bring about the bleaching activity. US 5360568 discloses
30 that imine quat molecules can be used to promote the activity of monopersulphate (an inorganic peroxygen compound) and peroxy-adipyl-phthalimide (PAP) (an organic peracid).

- 3 -

In the above-mentioned compositions the imine quat is believed to be converted, by reaction with the peracid into an oxaziradinium salt which can act as an oxygen donor (i.e. a bleaching species) and which is

- 5 converted back into the imine quat. The oxaziradinium ion is however unstable at high pH in the compositions described above, where it is believed to be converted into an acyl hydroxamate thereby preventing the bleaching cycle from working efficiently. As a
10 result, compositions have been limited in pH range and it has proved difficult to formulate compositions which are effective against the more recalcitrant stains particularly hydrophobic and/or pyrolysed stains.

15

Brief Description of the Invention

- 20 It is believed that the above-mentioned problem is overcome by the use of hydrogen peroxide, rather than an organic peracid or an inorganic peroxide, as the source of oxidising equivalents. This enables the formulation of compositions to bleach at relatively high pH's where some of the more difficult stains are
25 soluble and hence accessible to the formulation. Other, hitherto unsuspected benefits arise from the use of hydrogen peroxide as are described below.

- 30 Accordingly, the present invention provides a bleaching composition of pH 10-14 which comprises an oxygen transfer agent and hydrogen peroxide.

- 35 Without wishing to limit the scope of the present specification by reference to some theory of operation, it is believed that the reaction of

- 4 -

hydrogen peroxide with the imine quat. oxygen transfer agents proceeds through a different route than that of the organic and inorganic peroxides mentioned above.

As a consequence, the formation of acyl hydroxamate is

5 significantly reduced. Furthermore it is believed that when hydrogen peroxide is used as the bleaching agent in the pH range indicated, a surprising improvement in the efficacy of the bleaching system

10 occurs and it is possible to formulate peroxide based systems which have efficacy approaching or exceeding that of hypochlorite without the disadvantages associated with hypochlorite.

15 A further aspect of the present invention provides a method for bleaching a stained substrate which comprises the step of treating the substrate with a bleaching composition of pH 10-14 which bleaching composition comprises an oxygen transfer agent and hydrogen peroxide.

20

Detailed Description of the Invention

25 As noted above, hydrogen peroxide is an essential component of the compositions according to the present invention. As hydrogen peroxide is a reactive species, this will place some limitations on the other components which can be present. These are described in greater detail below.

30

Hydrogen peroxide is preferably present at a level of 0.5-10%wt on product, more preferably 1-5%wt on product. In typical embodiments of the invention the weight ratio of the hydrogen peroxide to the oxygen transfer agent falls in the range 5:1 to 20:1.

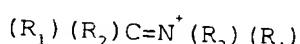
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- 5 -

Oxygen Transfer Agents

Oxygen transfer agents for use in the present invention, include, but are not limited to, the imine quat. N-methyl-3,4-dihydroisoquinolinium salts. Where these salts are used, suitable counter-ions include halides, sulphate, methosulphate, sulphonate, p-toluene sulphonate and phosphate. Oxygen transfer agents which comprise a quaternary nitrogen atom are preferred.

A broad class of oxygen transfer agents suitable for use in embodiments of the present invention are compounds comprising ions of the general structure:



Wherein:

R₁ and R₄ are in a *cis*- relation and are substituted or unsubstituted moieties selected from the group consisting of hydrogen, phenyl, aryl, heterocyclic ring, alkyl and cycloalkyl radicals;

R₂ is a substituted or unsubstituted moiety selected from the group consisting of hydrogen, phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nito, halo, cyano, alkoxy, keto, carboxylic acid and carboalkoxy groups;

30

R₃ is a substituted or unsubstituted moiety selected from the group consisting of hydrogen, phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nito, halo and cyano groups;

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Preferably, R₁ with R₂ and R₃, respectively together form a moiety selected from the group consisting of cycloalkyl, polycyclo, heterocyclic and aromatic ring systems.

5

Heterocyclic rings according to the present specification include cycloaliphatic and cycloaromatic type radicals incorporating an oxygen, sulphur and/or nitrogen atom within the ring system. Representative

10 nitrogen heterocycles include pyridine, pyrrole, imidazole, triazole, tetrazole, morpholine, pyrrolidone, piperidene and piperazine. Suitable oxygen heterocycles include furan, tetrahydrofuran and dioxane.

15 Sulphur heterocycles may include thiophene and tetrahydrothiophene.

The term substituted as used in relation to R₁, R₂, R₃ and R₄ includes a substituent which is nitro, halo, cyano, C1-C20 alkyl, amino, aminoalkyl, thioalkyl, 20 sulphonyl, carboxyester, hydroxy, C1-C20 alkoxy, polyalkoxy, or C1-C40 quaternary di- or tri-alkyl ammonium.

Preferred oxygen transfer agents are quaternary imine salts, particularly those set forth in US patent specification 5,360,568 (Madison and Coope), more particularly the substituted or unsubstituted isoquinolinium salts, preferably the 3,4 di-hydro isoquinolinium salts and more preferably the N-methyl 30 3,4 di-hydro-isoquinolinium salts. N-methyl 3,4 di-hydro-isoquinolinium p-toluene sulphonate is a particularly preferred oxygen transfer agent.

Typically, the oxygen transfer agents are present at 35 levels of 0.001-10%wt on product. Preferably, the

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oxygen transfer agents are present at levels of 0.01-1%wt on product, more preferably 0.1-0.5%wt on product.

5

Surfactants

It is preferred that the compositions according to the invention further comprise one or more surfactant species. Surfactants can be nonionic, anionic, cationic, amphoteric or zwitterionic provided that they, and where appropriate their counter-ions, do not react substantially with the oxygen transfer agent or the hydrogen peroxide.

15

Suitable nonionic detergent active compounds can be broadly described as compounds produced by the condensation of alkylene oxide groups, which are hydrophilic in nature, with an organic hydrophobic compound which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Particular examples include the condensation product of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut oil ethylene oxide condensate having from 3 to 10 moles of ethylene oxide per mole of coconut alcohol; condensates of alkylphenols whose alkyl group contains from 6 to 12

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carbon atoms with 3 to 10 moles of ethylene oxide per mole of alkylphenol.

- 5 The preferred alkoxylated alcohol nonionic surfactants are ethoxylated alcohols having a chain length of C9-C11 and an EO value of at least 3 but less than 10. Particularly preferred nonionic surfactants include the condensation products of C₁₀ alcohols with 3-8 moles of ethylene oxide. The preferred ethoxylated 10 alcohols have a calculated HLB of 10-16. An example of a suitable surfactant is 'IMBENTIN 91-35 OFA' (TM, ex. Kolb AG) a C₉₋₁₁ alcohol with five moles of ethoxylation.
- 15 Alternative surfactants include amine oxides, amines and/or ethoxylates thereof. Amine oxides with a carbon chain length of C12-C14 are particularly preferred.
- 20 When present, the amount of nonionic detergent active to be employed in the composition of the invention will generally be from 0.01 to 30%wt, preferably from 0.1 to 20%wt, and most preferably from 3 to 10%wt for non-concentrated products. Concentrated products will 25 have 10-20%wt nonionic surfactant present, whereas dilute products suitable for spraying will have 0.1-5%wt nonionic surfactant present.

pH

- 30 As noted above the pH of compositions according to the present invention falls in the range 10-14. pH of compositions is preferably 10-12, more preferably 10-11. At these higher pH's we have found that the 35 composition penetrates more readily into the soils.

As is noted in the illustrative examples given below, the use of oxygen transfer agents at high pH is contra-indicated by their tendency to increase the colour of a stain rather than reduce it.

5

Minors

Minor components of compositions according to the
10 present invention include those typically present in
cleaning compositions.

In compositions which contain hydrogen peroxide it is useful to include a metal ion complexing agent to
15 retard decomposition of the peroxide by any metal ions which may be present as contaminants or such as are introduced during processing. Again, these components should be selected such that they do not react do not react substantially with the oxygen transfer agent or
20 the hydrogen peroxide.

Preferably, cleaning and/or disinfecting compositions according to the invention will further comprise metal ion sequestrants such as ethylene-diamine-tetra-
25 acetates, amino-polyphosphonates (such as those in the DEQUEST (TM) range) and phosphates and a wide variety of other poly-functional organic acids and salts, can also optionally be employed. Preferred metal ion sequesterants are selected from dipicolinic acid,
30 ethylene diamine tetra acetic acid (EDTA) and its salts, hydroxy-ethylidene diphosphonic acid (Dequest 2010, RTM), ethylene diamine tetra (methylene phosphonic acid) (Dequest 2040, RTM), diethylene triamine penta(methylene phosphonic acid) (Dequest 35 2060, RTM), amino tri(methylene phosphonic acid)

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(Dequest 2000, RTM). The phosphonic acid derivatives are particularly preferred. It is preferred that the level of phosphonic acid derivative metal ion complexing agent should fall into the range 0.05-5%.

5

Preferably, cleaning and/or disinfecting compositions according to the invention will further comprise at least 1% of a solvent of the form $R_1-O-(EO)_m-(PO)_n-R_2$, wherein R_1 and R_2 are independently C2-6 alkyl or H,

10 but not both hydrogen, m and n are independently 0-5. More preferably, the solvent is selected from the group comprising di-ethylene glycol mono n-butyl ether, mono-ethylene glycol mono n-butyl ether, propylene glycol n-butyl ether, isopropanol, ethanol, 15 butanol and mixtures thereof. Typically, the level of solvent in cleaning and disinfecting compositions is 1-10%, with a solvent: nonionic ratio of 1:3-3:1 being particularly preferred.

20 Where compositions according to the present invention are liquids, they can be water-thin or thickened. Thickened compositions are advantageous in that they cling to sloping surfaces and find particular utility in toilet cleaners. Slight thickening of the 25 composition is desirable for applications in which the composition is sprayed, so as to reduce the extent to which small droplets are produced which might otherwise cause respiratory irritation to the user. Suitable thickening agents include amine oxide and 30 soap and systems based on nonionic surfactants.

Compositions according to the invention can also contain, in addition to the ingredients already mentioned, various other optional ingredients such as, 35 colourants, optical brighteners, soil suspending

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agents, deterotive enzymes, gel-control agents, freeze-thaw stabilisers, further bactericides, perfumes and opacifiers .

5 A particularly preferred compositions according to the present invention comprises a bleaching composition having a pH of 10-12, said composition being an aqueous liquid and comprising:

- 10 a) hydrogen peroxide at a level of 0.5-10%wt on product,
- b) 0.001-10%wt on product of an isoquinolinium salt,
- 15 c) 0.01 to 30%wt on product of at least one nonionic surfactant, and,
- d) optional minors selected from the group consisting of metal ion sequestering agents,
- 20 solvents and perfumes.

Product form

25 Products according to the present invention are generally liquids and preferably aqueous. However, other product forms including pastes and solids are also envisaged.

30 As will be appreciated, the product form is largely determined by the end use and consequently liquids are generally suitable for use as hard surface cleaners, including cleaners for industrial, institutional and domestic cleaning and/or disinfection of hard surfaces

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including metal, plastics materials or other polymers, ceramic, and glass surfaces.

It is envisaged the method of the present invention
5 can be applied in the cleaning of surfaces used for
the preparation of food and beverages (e.g. worktops,
conveyor systems and utensils) or other industrial,
institutional and domestic surfaces such as sanitary
ware, industrial, institutional and domestic fluid
10 supply applications, for disinfection of medical,
surgical or dental apparatus, equipment, facilities or
supplies, catheters, contact lenses, surgical dressings
or surgical instruments, in horticultural
applications, e.g. for sterilising the surfaces of
15 greenhouses, for soft surfaces including fabrics
(including in dressings, wipes and cloths), and non-
living materials of biological origin (such as wood).
Solid product forms are suitable for use as toilet and
urinal blocks and other uses where slow or delayed
20 release of the components is required.

In order that the present invention may be further
understood it will be described hereinafter by
reference to illustrative and non-limiting examples
25 and comparisons.

EXAMPLES

30 The following examples were performed using model
kitchen soils and a soiling procedure as described
below. The soils were chosen to have recalcitrant
stains, which would be difficult to bleach due to the
hydrophobic or pyrolysed nature of the stain.
35

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Example 1: Curcumin/oil stain on formica (TM).

Soil preparation

- 5 Flat tiles, measuring 4" x 4", are cut from white
Formica sheeting and their surfaces thoroughly cleaned
using a commercially available liquid abrasive
cleaner, 'Jif' (TM). After rinsing with demineralised
water, the tiles are allowed to dry at room
10 temperature.

The curcumin/oil stain is prepared by mixing 19 g of
vegetable oil and 180 g of ethanol and then adding 1 g
of pure curcumin (a pigment found in curry powder).

- 15 After thorough stirring, the resulting solution is
sprayed onto the tiles using an airbrush propellant
canister so as to give a uniform surface coverage.
The tiles are left to dry for a minimum of 10 minutes,
during which time the ethanol evaporates leaving a
20 bright yellow, slightly sticky, oily stain, which
cannot be removed by wiping or rinsing with water.
Curcumin is susceptible to photo-oxidation and stained
tiles should not be stored for periods exceeding 2
hours before use.

25

Preparation of Bleach or Surfactant Solutions

- Experiments were performed with hydrogen peroxide, PAP
30 (peroxy-adipoyl-phthalimide), peroxymonosulphate and
sodium hypochlorite (a well known inorganic bleaching
agent).

- Bleach solutions are prepared by dissolving the
35 peroxide co-oxidant in demineralised water and, where

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necessary, adding the oxygen transfer agent. Sodium hydroxide solution (5 mol dm⁻³) is added dropwise to adjust the pH to the desired value, as determined using a pH meter. Further demineralised water is
5 added to the solution to give the desired final volume.

In the examples described the oxygen transfer agent was N-methyl 3,4 di-hydro isoquinolinium p-toluene
10 sulphonate. The preparation of this material is described in US 5360569 and US 5360568 which are incorporated herein by reference. The material is referred to below as the 'Imine Quat'.

15 Hydrogen peroxide solutions are prepared to achieve a final concentration of 3 w/w % (0.88 mol dm⁻³) and used in conjunction with a 1% molar equivalency of the Imine Quat catalyst (0.0088 mol dm⁻³, 0.30 w/w %). Solutions of potassium Caroate (TM: 6 w/w%, equivalent
20 to 3 w/w%, 0.2 mol dm⁻³ peroxomonosulphate) and PAP (6-[N-phthalimido]-perhexanoic acid: 2 w/w%, 0.012 mol dm⁻³) were examined in combination with the same level of Imine Quat. The potassium peroxyomonosulphate system was examined at pH 8.5 (but higher pH values
25 were used for hydrogen peroxide (which has a higher pK_a) and PAP (which is relatively insoluble at lower alkalinitities). Addition of a wetting agent (1% butyl digol (TM): diethylene glycol mono n-butyl ether) further increases the PAP solubility.
30

The bleach systems are compared with the detergency obtained using a C₉₋₁₁ EO₅ nonionic surfactant, Imbentin 91-35 OFA (TM) in the formulations listed in TABLE 1 below. In some instances a solvent 'Butyl Digol'

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(TM), di-ethylene glycol mono-n-butyl ether, was added or used for comparison.

5 Soil removal experiments

Examples were performed at room temperature. A glass ring, of diameter 50 mm and height 15 mm, is placed over the centre of the stained tile and 5 cm³ of the aqueous bleach or surfactant solution is pipetted within the annulus of the ring. The solution is allowed to remain in contact with the stained tile surface for 30 seconds, after which the glass ring is removed and the solution poured away. The tile is immediately rinsed with demineralised water for a further 30 seconds and then allowed to dry. Each solution is used to treat two tiles.

The extent of stain removal is assessed visually by a panel of at least 15 people, using a standard scale. Tiles are graded on an integer scale ranging from 0 to 5, where 0 denotes no visible soil removal and 5 corresponds to total removal. A minimum of two stained tiles are treated with each bleach solution and mean scores for each system are calculated by averaging the scores from both tiles.

Results are shown in TABLE 1 below. From the results presented in TABLE 1, it can be seen that a significant improvement as regards hydrogen peroxide bleaching is obtained in the presence of the Imine Quat at both pH 10 and pH 10.5. A similar increase is not seen for either the organic or inorganic peroxy acid.

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Comparing the results with conventional
cleaning/bleaching systems. It can be seen that use
of an oxygen transfer agent together with hydrogen
peroxide provides results which are very favourably
5 comparable with hypochlorite, and significantly better
than alkali and surfactant based systems.

TABLE 1

System	Without Imine Quat.	With 0.3% Imine Quat
3% Hydrogen Peroxide at pH 10.0	0.1	1.3
3% Hydrogen Peroxide at pH 10.5	1.3	3.1
2% PAP/1% Butyl Digol at pH 10.0	0.1	0.3
3% K-monoperoxyxysulphate at pH 8.5	0	0
1% NaOCl at pH 10	2.9	-
1% NaOCl at pH 10.5	3.8	-
Alkali at pH 10.0	0.2	-
Alkali at pH 10.5	1.6	colour of stain increased
0.1% Imbentin at pH 10.0	1.0	-
0.1% Imbentin at pH 10.5	1.5	-

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Example 2: Baked fat/flour on enamel

Soil preparation

- 5 Oleic acid (1 g), stearic acid (1 g) and Friol (TM)
Italian Oil (38 g) are mixed in a metal beaker and
directly heated, using a hotplate, to a temperature of
60°C, so that the mixture liquifies. Demineralised
water (100 g) is boiled and allowed to cool to 60°C
10 before mixing with Italian flour (40 g) to make a
thick paste.

- The organic acid-oil mixture and the flour paste are
placed in a liquidiser jug and demineralised water
15 (280 g) added. The fat-flour mixture is blended for 5
seconds, allowed to stand for 10 seconds and then
blended for a further 5 seconds. The contents of the
liquidiser are then transferred to a glass beaker and
gently warmed by direct heating over a hot-plate. The
20 mixture is allowed to simmer for five minutes with
constant agitation from an overhead stirrer. The
mixture must not be allowed to stick to the beaker or
excessive cross-linking will occur, resulting in a
soil that is overly resistant to removal. The mix is
25 then transferred to a polythene beaker and allowed to
cool before use.

Soil application

- 30 White enamel tiles (100 mm x 100 mm) are cleaned using
a commercially available liquid abrasive cleaner
('Jif' [TM]), rinsed in demineralised water and
allowed to dry. The tiles are then coated with a thin
35 (c.a. 0.5 mm) layer of the fat/flour mix using a

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screen printing technique. A flexible rubber paddle is used to spread the mix onto the tile surface, through a thin plastic mesh, taking care to achieve a uniformly thin coverage. The soiled tiles are allowed
5 to stand overnight in the open air, acquiring a uniform matt finish. The tiles are baked on the middle shelf of an oven at 190°C for one hour, developing a light brown colouration, and allowed to cool for 2 hours before cleaning. As there is
10 expected to be variation between batches of these tiles soiled and subsequently pyrolysed, it is important that comparisons are performed with tiles taken from the same batch.

15

Preparation of Bleach and Surfactant Solutions

Solutions are prepared as described for the curcumin-oil soil removal experiments described above with
20 reference to TABLE 1 using the formulations listed in TABLE 2 below. Detergency effects have been studied using Neodol 91-5 (TM) nonionic surfactant, a commercially available, slightly less pure, version of the Imbentin 91-35 OFA (TM) surfactant used in the
25 curcumin/oil experiments above. Admox 10 (TM) is a C₁₀ amine oxide surfactant.

Peracetic acid is used at a concentration equal to that of the HOO⁻ active oxidising species present in
30 the 3% hydrogen peroxide solution at the same pH (10.0).

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Soil removal experiments

Soil removal is carried out using a standard Wool Industries Research Association Abrasion Tester (WIRA:

5 TM) apparatus. Two soiled tiles are cleaned simultaneously with the same solution, to provide duplicate results. The bleach or surfactant solution (20 cm³) is poured onto the surface of the tile, and rubbed using a cleaning head covered with two layers 10 of clean 'J'-cloth (TM) material. Each tile is cleaned using 51 strokes of the head. The tiles are then immediately removed from the apparatus, rinsed under running water and patted dry using paper tissues.

15

As noted above, although the colouration and ease of soil removal is uniform for tiles coated with a specific fat-flour mixture, there is some variability between different batches of soil. Consequently, the 20 results shown below in TABLE 2 are grouped in sets (TABLE 2a, 2b and 2c), each carried out using a different batch of fat-flour soiled tiles.

Experiments using Jif (TM) liquid abrasive cleaner and Domestos Multi-Surface Cleaner (TM), a commercial 25 hypochlorite hard surface cleaning product, are included in each series of runs to provide reference standards. The extent of soil removal is assessed visually by a panel of at least 5 people, using a standard scale. Tiles are graded on a scale ranging 30 from 0 to 10, and panellists award integer or half-integer scores to each tile. A score of 0 denotes no visible soil removal and 10 corresponds to total soil removal. Mean scores for each soil removal system are calculated by averaging scores from both replicates.

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Comparing the results with conventional cleaning/bleaching systems, it can be seen that use of an oxygen transfer agent together with hydrogen peroxide provides results which are very favourably

5 comparable with hypochlorite and commercial products based on hypochlorite, and which are significantly better than alkali and surfactant based systems. It can be seen from table 2d that while the imine quat shows a reduced effect in the presence of surfactant,

10 the improvement over systems which do not contain the imine quat. is still measurable.

TABLE 2a

System	Without Imine Quat.	With 0.3% Imine Quat
3% Hydrogen Peroxide at pH 10.5	8.5	9.0
3% K-monoperoxysulphate at pH 8.5	5.6	5.6
Domestos Multi Surface Cleaner at pH 11.5	10	-
JIF at pH 11.0	5.8	-
Alkali at pH 10.5	6.4	-
0.1% Neodol at pH 10.5	3.5	-

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TABLE 2b

System	Without Imine Quat.	With 0.3% Imine Quat.
3% Hydrogen Peroxide at pH 10.0	3.9	4.9
0.12% peracetic acid at pH 10.0	2.9	3.8
Domestos Multi Surface Cleaner at pH 11.5	9.1	-
JIF at pH 11.0	3.6	-

5

TABLE 2c

System	Without Imine Quat.	With 0.3% Imine Quat
3% Hydrogen Peroxide at pH 10.0	7.2	9.1
Domestos Multi Surface Cleaner at pH 11.5	10	-
3% NaOCl at pH 10.0	8.1	-

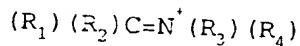
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TABLE 2d

System	Without Imine Quat.	With 0.3% Imine Quat
3% Hydrogen Peroxide at pH 10.0	7.5	8.0
3% Hydrogen Peroxide & 0.1% Admox 10 at pH 10.0	7.3	7.9
Domestos Multi Surface Cleaner at pH 11.5	9.4	-
JIF at pH 11.0	4.3	-

CLAIMS

- 5 1. A bleaching composition of pH 10-14 which
comprises an oxygen transfer agent and hydrogen
peroxide.
- 10 2. A bleaching composition according to claim 1
wherein hydrogen peroxide is present at a level
of 0.5-10%wt on product.
- 15 3. A bleaching composition according to claim 1
wherein the weight ratio of the hydrogen peroxide
to the oxygen transfer agent falls in the range
5:1 to 20:1.
- 20 4. A bleaching composition according to claim 1
wherein the oxygen transfer agent is a compound
comprising ions of the general structure:



25 wherein:

25

R₁ and R₄ are in a *cis*- relation and are
substituted or unsubstituted radicals selected
from the group consisting of hydrogen, phenyl,
aryl, heterocyclic ring, alkyl and cycloalkyl
radicals.

30

R₂ is a substituted or unsubstituted radical
selected from the group consisting of hydrogen,
phenyl, aryl, heterocyclic ring, alkyl,

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cycloalkyl, nito, halo, cyano, alkoxy, keto,
carboxylic acid and carboalkoxy groups; and,

R_j is a substituted or unsubstituted radical
selected from the group consisting of hydrogen,
phenyl, aryl, heterocyclic ring, alkyl,
cycloalkyl, nito, halo and cyano groups:

5. A bleaching composition according to claim 4
10 wherein the oxygen transfer agent is a
substituted or unsubstituted isoquinolinium salt.
6. A bleaching composition according to claim 1
15 having a pH of 10-12, said composition being an
aqueous liquid and comprising:
 - a) hydrogen peroxide at a level of 0.5-10%wt on
product,
 - 20 b) 0.001-10%wt of product of an isoquinolinium
salt,
 - c) 0.01 to 30%wt on product of at least one
nonionic surfactant, and,
 - 25 d) optional minors selected from the group
consisting of metal ion sequestering agents,
solvents and perfumes.
- 30 7. A method for bleaching a stained substrate which
comprises the step of treating the substrate with
a bleaching composition as defined in any one of
claims 1-6.

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